1 409 009

PATENT SPECIFICATION

(11) 1 409 009

(21) Application No. 59232/73 (22) Filed 20 Dec. 1973
(31) Convention Application No. 127999/72
(32) Filed 20 D c. 1972 in
(33) Japan (JA)
(44) Complete Specification published 8 Oct. 1975
(51) INT CL² G03C 1/08//C07C 53/24; C07D 249/18
(52) Index at acceptance
G2C 212 242 26Y 304 30X 321 326 362 371 C19E2A C19HX C19Y
C2C 1452 20Y 213 247 250 252 25Y 292 29Y 30Y 366 367 37X 628 67Y 69Y 77Y 798 79Y CM ZG

(19)

(54) THERMALLY DEVELOPABLE LIGHT-SENSITIVE MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a heat-developable light-sensitive material.

Heretofore, photographic methods using silver halide have been widely practiced, since silver halides provide [illegible]

ERRATA

SPECIFICATION No. 1,409,009

Page 7, line 10, *for* monosulphate *read* monosulphonate
Page 12, line 23, *after* (C) *insert* was
Page 13, line 25, *for* 2-(*p*-dimethylaminostryryl) *read* 2-(*p*-dimethylaminostyryl)

THE PATENT OFFICE
1st December, 1975

[illegible]sulphonate), or of saccharin, or of benzotriazole, and a catalytic amount of a silver halide. The present invention relates to this recent proposal.

Heat-developable light-sensitive materials so far proposed are unfortunately insufficiently light-sensitive. It is however known that merocyanine dyes, the so-called colour sensitizers for silver halide emulsions, can also sensitize heat-developable light-sensitive materials.

Nonetheless, not all colour sensitizing agents effective for silver halide emulsions are necessarily effective for a heat-developable light-sensitive material.

We have discovered that a quinoline compound represented by the general formula (I) hereinafter described and certain derivatives thereof show good sensitizing effects for certain heat-developable light-sensitive materials.

Thus the present invention consists in a heat-developable light-sensitive material comprising a support bearing:

(a) an organic silver salt,

(b) a light-sensitive silver halide, or a compound capable of forming a light-

SEE ERRATA SLIP ATTACHED

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(54) THERMALLY DEVELOPABLE LIGHT-SENSITIVE MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a heat-developable light-sensitive material.

Heretofore, photographic methods using silver halide have been widely practiced, since silver halides provide excellent sensitivity and gradation compared with electrophotographic methods or diazo-type photographic methods.

However, a silver halide light-sensitive material which is used in this method must, after imagewise exposure, be developed and then subjected to stopping, fixing, washing and stabilizing, in order to prevent the developed image from discolouring or fading and also to prevent the non-developed area (hereinafter referred to as "background") from blackening. Much time and labour are incurred and operators are exposed to danger from handling the necessary chemicals, and their hands and clothes may become stained.

Therefore, it would be desirable to process silver halide material in a dry state such that the processed images could be maintained stable.

Various proposals have been made to this end, for instance a combined developing and fixing method described in U.S. Patent 2,875,048, British Patent No. 954,453 and Federal German Patent No. 1,163,142, and a proposal to substitute dry processing operations for the wet processing operations in the conventional silver halide photographic method, as described in Federal German Patent No. 1,174,159 and British Patent Nos. 943,476 and 951,644. A recent proposal, as described in Japanese Patent Publication No. 22185/70, U.S. Patents 3,152,904, 3,457,075, 3,635,719 and 3,645,739 and British Patent No. 1,205,000, is to use a heat-developable light-sensitive material containing a light-sensitive element comprising mainly a silver salt such as a long-chain carboxylic acid (e.g. silver behenate), of saccharin, or of benzotriazole, and a catalytic amount of a silver halide. The present invention relates to this recent proposal.

Heat-developable light-sensitive materials so far proposed are unfortunately insufficiently light-sensitive. It is however known that merocyanine dyes, the so-called colour sensitizers for silver halide emulsions, can also sensitize heat-developable light-sensitive materials.

Nonetheless, not all colour sensitizing agents effective for silver halide emulsions are necessarily effective for a heat-developable light-sensitive material.

We have discovered that a quinoline compound represented by the general formula (I) hereinafter described and certain derivatives thereof show good sensitizing effects for certain heat-developable light-sensitive materials.

Thus the present invention consists in a heat-developable light-sensitive material comprising a support bearing:

(a) an organic silver salt,

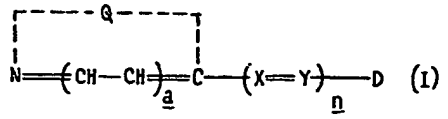
(b) a light-sensitive silver halide, or a compound capable of forming a light-

sensitive silver halide by reaction with said organic silver salt (a), in an amount effective to catalyze the reaction of compounds (a) and (c),

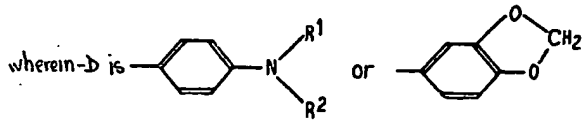
(c) a reducing agent capable of reducing to elemental silver the organic silver salt (a) when the material is being heated in the presence of the component (b) which has been exposed to light,

(d) a bind r, which may be omitted if the organic silver salt (a) and/or the reducing agent (c) act as a binder,

(e) a quinoline compound represented by the following general formula (I):



(I)

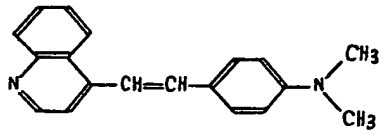


R^1 and R^2 being each independently an alkyl group having from 1 to 4 carbon atoms or a benzyl group; X and Y are each independently $=\overset{H}{C}-$ or $=N-$; n is 1 or 2; a is 0 or 1; and Q represents the atoms necessary to complete a quinoline nucleus which may be further substituted; or (e) may be a quinoline ring N-oxide derived from said quinoline compound or a quinolinium salt derived from said quinoline compound.

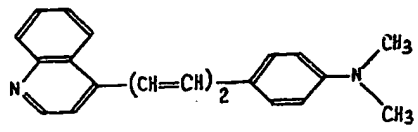
R^1 and R^2 are preferably methyl, ethyl or propyl such as *n*-propyl. R^1 and R^2 can be the same or different. Also, the quinoline nucleus in the general formula can be substituted, such as by an alkyl group having 1 to 4 carbon atoms, such as methyl, ethyl, isopropyl or isobutyl (any of which may be substituted with a halogen atom or a hydroxyl group, thus being e.g. hydroxyethyl or β-chloroethyl), a phenyl group, an alkoxy group having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy or butoxy, a halogen such as a fluorine, chlorine, bromine or iodine, a dialkylamino group in which the alkyl moiety may have 1 to 4 carbon atoms (e.g. methyl, ethyl, propyl, isopropyl, butyl or *t*-butyl), an alkoxycarbonyl group having 1 to 4 carbon in the alkoxy moiety (such as a methoxycarbonyl or ethoxycarbonyl group) and $-(X=Y)_n-D$, X, Y, *n* and D being as hereinbefore defined in connection with the general formula (I).

Now, specific examples of the compounds represented by the general formula (I), quinoline ring N-oxides thereof and quinolinium salts thereof, useful as the sensitizing agent in the present invention, are given below:

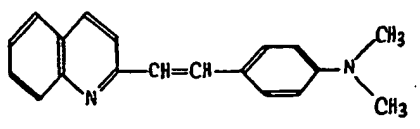
(1) 4-(*p*-dimethylaminostyryl)quinoline



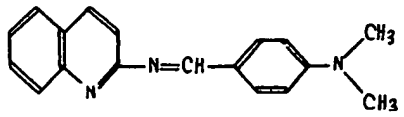
(2) 4-(4-*p*-dimethylaminophenyl-1,3-butadienyl)quinoline



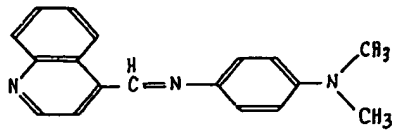
(3) 2-(4-dimethylaminostyryl)quinoline



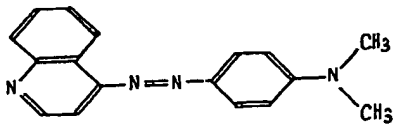
(4) 2-(*p*-dimethylaminobenzylidene)aminoquinoline



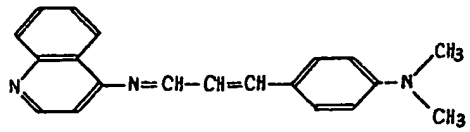
(5) 4-(*p*-dimethylaminophenylimino)methylquinoline



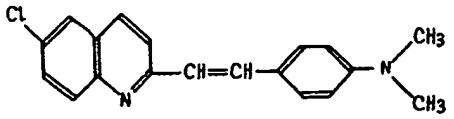
(6) 4-(*p*-dimethylaminophenylazo)quinoline



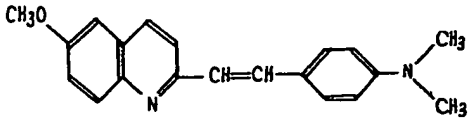
(7) 4-[(3-*p*-dimethylaminophenyl)-2-propenylidene]-aminoquinoline



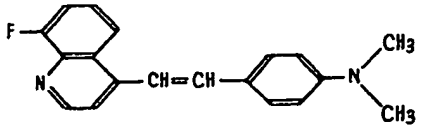
(8) 6-chloro-2-(*p*-dimethylaminostyryl)quinoline



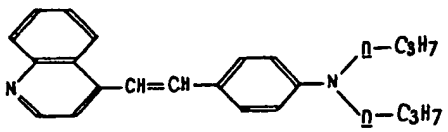
(9) 6-methoxy-2-(*p*-dimethylaminostyryl)quinoline



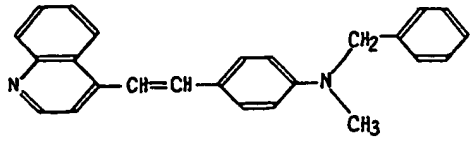
(10) 8-fluoro-4-(*p*-dimethylaminostyryl)quinoline



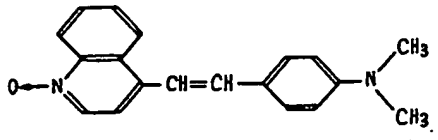
(11) 4-(*p*-dipropylaminostyryl)quinoline



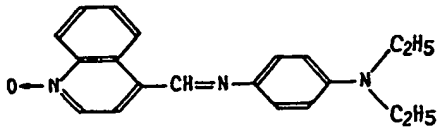
(12) 4-(*p*-methylbenzylaminostyryl)quinoline



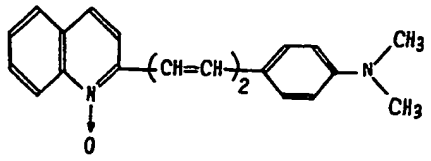
(13) 4-(*p*-dimethylaminostyryl)quinoline-1-oxide



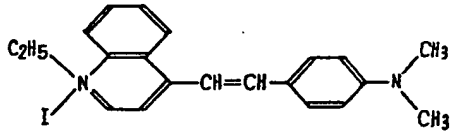
(14) 4-(*p*-diethylaminophenylimino)methylquinoline-1-oxide



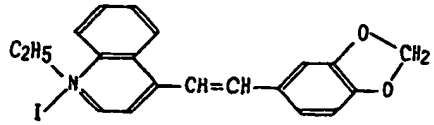
(15) 2-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]quinoline-1-oxide



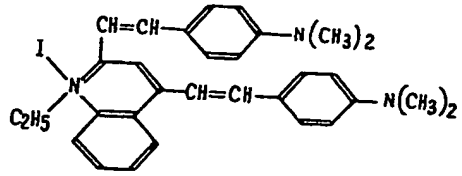
(16) 4-(*p*-dimethylaminostyrylquinolinium) ethyl iodide



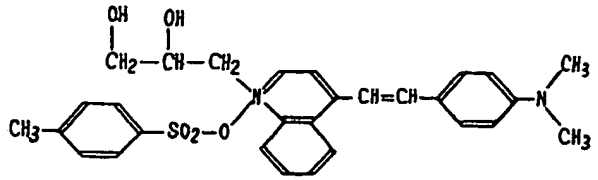
(17) 4-(3,4-dioxymethylenephenylethylenyl)quinolinium ethyl iodide



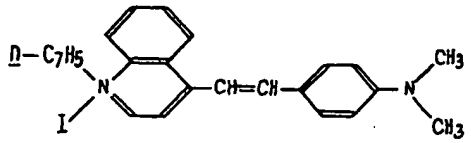
(18) 2,4-*bis*(*p*-dimethylaminostyryl)quinolinium ethyl iodide



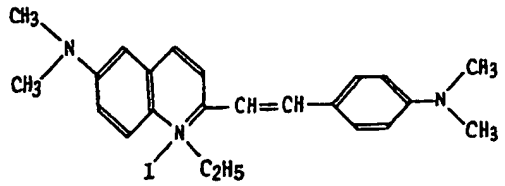
(19) 4-(*p*-dimethylaminostyryl)quinolinium 1,2-dihydroxypropyl tosylate



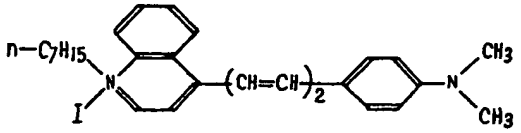
(20) 4-(*p*-dimethylaminostyryl)quinolinium *n*-heptyl iodide



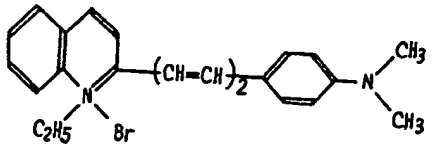
(21) 2-(*p*-dimethylaminostyryl)-6-dimethylaminoquinolinium ethyl iodide



(22) 4-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]quinolinium *n*-heptyl iodide



(23) 2-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]quinolinium ethyl bromide



These compounds can be used alone or in combinations of two or more. Compounds (1), (17), (20), (21), and (22) are particularly preferred.

The compound effective as the sensitizing agent in material according to the present invention (component (e)) is suitably added in an amount of from 10^{-6} mol to 10^{-2} mol, preferably 10^{-5} mol to 10^{-3} mol, per 1 mol of the organic silver salt (a), the amount chosen depending for example upon the kind of compound used, the kind of organic silver salt, the kind of silver halide, the kind of reducing agent and the processing temperature. If the amount of the component (e) exceeds 10^{-2} mol per mol of organic silver salt, and the component (e) is one giving rise to considerable density of colour, the degree of colouration of the light-sensitive layer can become too great, which is not desirable for some uses.

Suitable examples of organic silver salts which can be used as component (a) in the present invention are the silver salts of organic compounds having an imino group or a mercapto group, and the silver salts of organic (preferably carboxylic) acids, as disclosed in U.S. Patent 3,457,075. Silver salts of organic acids having 10 or more carbon atoms are preferable.

Specific examples of these silver salts include th silver salt of benzotriazole, of saccharin, of phthalazinone, of 3-mercapto-4-phenyl-1,2,4-triazole, of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, of 2-(S-ethylthioglycolamido)-benzothiazole, silver caprate, silver laurate, silver myristate, silver palmitate, silver stearate, silver behenate, silver adipate and silver sebacate.

Examples of component (b) in the present invention, capable of forming a light-sensitive silver halide by the reaction thereof with the organic silver salt (a), include hydrogen halide, ammonium halide or a metal halide, the metal preferably being strontium, cadmium, zinc, tin, chromium, sodium, barium, iron, caesium, lanthanum, copper, calcium, nickel, magnesium, potassium, aluminium, antimony, gold, cobalt, mercury, lead, beryllium, lithium, manganese, gallium, indium, platinum, thallium or bismuth, and the halide being the chloride, bromide or iodide.

Other examples of component (b) are organic halogen compounds such as monochlorotriphenylmethane, monobromotriphenylmethane, 2-bromo-2-methylpropane, 2-bromobutyric acid, 2-bromoethanol, dichlorobenzophenone, triiodomethane, tribromomethane and tetrabromomethane.

Suitable silver halides for use as component (b) are silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, silver chlorobromoiodide, silver chlorobromide and silver iodide. These light-sensitive silver halides can be of coarse grains or of fine grains. Emulsions of extremely fine grains are particularly useful.

Emulsions containing a light-sensitive silver halide (b) can be prepared in any conventional manner. Exemplary emulsions are produced using the single jet method, the double jet method (e.g. a Lippmann's emulsion), or are an ammoniacal emulsion, a thiocyanate- or thioether-ripened emulsion, or are as described in, e.g. U.S. Patents 2,222,264, 3,320,069 and 3,271,157.

Silver halides (b) used in material according to the present invention can be sensitized with conventional chemical sensitizers such as reducing agents, sulphur, selenium compounds, gold compounds, platinum compounds, palladium compounds, or combinations thereof. Suitable procedures for chemical sensitization are described in, e.g. U.S. Patent 2,623,499, 2,399,083, 3,297,447 and 3,297,446.

The compounds which can be employed as component (b) may be used independently or as a combination of two or more. This component (b) is suitably added in an amount of from 0.001 mol to 0.5 mol per 1 mol of the organic silver salt, component (a). If the amount of the component (b) is less than 0.001 mol per mol of (a), the sensitivity is reduced, while if it exceeds 0.5 mol per mol of (a), the non-image areas of the heat-developed material may gradually blacken upon leaving the material open to light, diminishing the contrast between the image areas and non-image areas.

The reducing agent which is used as component (c) in the present invention must be capable of reducing the organic silver salt (a) to form elemental silver images upon heating the light-sensitive material in the presence of the exposed component (b), which is a silver halide catalyst or can form such.

The best reducing agent for a particular material depends upon the organic silver salt used. For example, when using a silver salt of a higher fatty acid such as silver behenate, or using the silver salt of benzotriazole, which are comparatively difficult to reduce, comparatively strong reducing agents such as a *bis*-phenol (e.g. 4,4'-methylene*bis*-(3-methyl-5-*t*-butylphenol) or an ascorbic acid respectively are suitable. On the other hand, comparatively weak reducing agents such as a substituted phenol (e.g., *p*-phenylphenol) are suitable for silver salts which are comparatively easy to reduce, such as silver laurate. Examples of frequently useful reducing agents are substituted phenols, substituted or unsubstituted *bis*-phenols, substituted or unsubstituted naphthols, substituted or unsubstituted *bis*-naphthols, di- or poly-hydroxynaphthalenes, di- or higher-polyhydroxybenzenes, di- or higher-polyhydroxynapthalenes, hydroquinone monoethers, di-ethers, tri-ethers and tetra-ethers, ascorbic acid or derivatives thereof, 3-pyrazolidone, pyrazolin-5-ones, reducing saccharides (sugars), kojic acid and hinokitiol.

Preferred substituted phenols, bisphenols, bisnaphthols and naphthols are those where the substituent groups are alkyl (C_1—C_8), alkoxy (C_1—C_8), phenyl, halogen, amino, alkyl substituted amino (C_1—C_8), benzyl, hydroxyalkyl (C_1—C_8), acetyl or nitro.

Most preferred of the hydroquinone ethers are the monoalkyl (C_1—C_8) ethers, the monoaralkyl ethers and the monoaryl ethers.

Most preferred of the ascorbic acid derivatives are mono- or di-carboxylic acid esters of ascorbic acid.

Most preferred of the 3-pyrazolidones are substituted or non-substituted 1-aryl-3-pyrazolidones, wherein the substituents are preferably those described for the preferred substituted phenols.

Preferred of the pyrazoline-5-ones are again those with substituents as described for the preferred substituted phenols.

Specific examples of useful reducing agents (c) are: hydroquinone, methylhydroquinone, chlorohydroquinone, bromohydroquinone, phenylhydroquinone, hydroquinone monosulphate, *t*-octylhydroquinone, *t*-butylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, *p*-methoxyphenol, *p*-ethoxyphenol, hydroquinone monobenzyl ether, catechol, pyrogallol, resorcin, *p*-aminophenol, *o*-aminophenol, N-methyl-*p*-aminophenol, 2-methoxy-4-aminophenol, 2,4-diaminophenol, 2-*β*-hydroxyethyl-4-aminophenol, *p*-*t*-butylphenol, *p*-*t*-amylphenol, *p*-cresol, 2,6-di-*t*-butyl-*p*-cresol, *p*-acetophenol, *p*-phenylphenol, *o*-phenylphenol, 1,4-dimethoxyphenol, 3,4-xylenol, 2,4-xylenol, 2,6-dimethoxyphenol, sodium 1-amino-2-naphthol-6-sulphonate, 1-naphthylamine-7-sulphonic acid, 1-hydroxy-4-methoxynaphthalene, 1-hydroxy-4-ethoxy-naphthalene, 1,4-dihydroxy-naphthalene, 1,4-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1-hydroxy-4-aminonaphthalene, 1,5-dihydroxynaphthalene, 1-hydroxy-2-phenyl-4-methoxynaphthalene, 1-hydroxy-2-methyl-4-methoxynaphthalene, *α*-naphthol, *β*-napthol, 1,1'-dihydroxy-2,2'-binaphthyl, 4,4'-dimethoxy-1,1'-dihydroxy-2,2'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl, *bis*(2-hydroxy-1-naphthyl)methane, bisphenol A, 1,1-*bis*-(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 2,4,4-trimethylpentyl-*bis*-(2-hydroxy-3,5-dimethylphenyl)methane, *bis*(2-hydroxy-3-*t*-butyl-5-methylphenyl)-methane, *bis*(2-hydroxy-3,5-di-*t*-butylphenyl)methane, 4,4'-methylene*bis*(3-methyl-5-*t*-butylphenol), 4,4'-methylene*bis*(2,6-di-*t*-butylphenol), 2,2'-methylene*bis*(2-*t*-butyl-4-ethylphenol), 2,6-methylene*bis*(2-hydroxy-3-*t*-butyl-5-methylphenyl)-4-methylphenol, 3,3', 5,5'-tetra-*t*-butyl-4,4'-dihydroxy-biphenyl, l-ascorbic acid, l-ascorbic acid monoester, l-ascorbic acid diester, *p*-hydroxyphenylglycine, N,N-diethyl-*p*-phenylenediamind, furoin, benzoin, dihydroxyacetone, glycerinaldehyde, rhodizonic acid, tetrahydroxyquinone, methyl gallate, propyl gallate, hydroxytetronic acid, N,N-di(2-ethoxyethyl)hydroxylamine, glucose, lactose, 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, *bis*(3-methyl-4-hydroxy-5-*t*-butylphenyl)sulphide, 3,5-di-*t*-butyl-4-hydroxybenzyldimethylamine, and *α*,*α*-(3,5-di-*t*-butyl-4-hydroxyphenyl)-dimethyl ether.

These reducing agents can also be used in combinations of two or more.

The amount of the reducing agents which can be used in material according to the present invention depends upon the organic silver salt (a) used and also on the individual reducing agent. Generally speaking, in many cases an appropriate amount of the reducing agent is 0.1 to 5 mols per 1 mol of the organic silver salt (a).

In the present invention, components (a), (b), (c) and (e) are preferably dispersed in a binder (d), which may be conventional, and are borne on a support. Where the component (a) or (c) which is used is a high molecular weight material which is capable of functioning as a binder, the binder (d) as a separate component can be omitted.

Although hydrophobic binders are usually preferable, hydrophilic ones can also be used. Preferable binders are transparent or semitransparent and examples are natural substances such as gelatin, gelatin derivatives, a mixture thereof with latex-type vinyl polymers, cellulose derivatives, and synthetic polymer materials. Specific examples of such synthetic polymer materials include polyvinyl butyral, cellulose acetate butyrate, cellulose acetate propionate, polymethyl methacrylate, polyvinyl pyrrolidone, polystyrene, ethyl cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymer, vinyl chloride-vinyl acetate copolymer, vinyl acetate-vinyl chloride-maleic acid copolymer, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate phthalate, polyacrylamide and phthalated gelatin.

The ratio of the weight of binder (d) to the weight of organic silver salt (a) is suitably from 4:1 to 1:4.

The support which can be used in material according to the invention can be of any of a wide variety of conventional substances, for example cellulose ester film, poly(vinylacetal) film, polystyrene film, polyethylene terephthalate film, polyvinyl carbonate film, glass, paper or metal. A suitable total coating amount is

from 0.2 to 3 g of silver per square metre of the support, preferably 0.4 to 2 g of silver per square metre.

An antistatic layer or an electroconductive layer can be provided on the heat-developable light-sensitive material of the present invention if desired. Also, an antihalation substance or an antihalati n dye can be incorporated therein, as disclosed in British Patents 1,276,727 and 1,261,102.

If desired, a matting agent such as starch, titanium dioxide, zinc oxide or silica, as well as a fluorescent brightening agent such as a stilbene, triazine, oxazole or coumarin can be additionally incorporated in the material.

The components (a) to (e) and any additives can be applied on a support, to form a heat-developable light-sensitive material according to the invention, using various coating methods including immersing methods, air-knife coating methods, curtain-coating methods and extrusion coating methods using a hopper as described in U.S. Patent 2,681,294. If desired, two or more layers can be applied at the same time. The components (a) to (e) and any additives may be present in a single layer or some may be applied as separate layers.

Some optically sensitizing dyes used for silver halide emulsions can increase the light sensitivity of the heat-developable light-sensitive material of the present invention. Useful optical sensitizers include the cyanine dyes and the merocyanine dyes, as disclosed in U.S. Patents 3,457,075 and 3,761,279. The amount used of the cyanine or merocyanine dyes is preferably from 10^{-6} mol to 10^{-2} mol per 1 mol of the organic silver salt (a).

In order to enhance the transparency of the thermally developable light-sensitive layer, to increase the image density and to improve the shelf-life of the material, a top-coating polymer layer, preferably 1 to 20 microns thick, can be provided on the light-sensitive layer. Suitable top-coating polymers include polyvinyl chloride, polyvinyl acetate, vinyl chloridevinyl acetate copolymers, polyvinyl butyral, polysturene, polymethyl methacrylate, polyurethane rubbers, xylene resins, benzyl cellulose, ethyl cellulose, cellulose acetate butyrate, cellulose acetate, polyvinylidene chloride, chlorinated polypropylene, polyvinyl pyrrolidone, cellulose propionate, polyvinyl formal, cellulose acetate phthalate, polycarbonates and cellulose acetate propionate.

Heat-developable light-sensitive material according to the invention can be developed, after being exposed to irradiation in the ultraviolet and/or visible range from a xenon lamp, tungsten lamp, mercury lamp, or other light source, by merely heating the light-sensitive material. Heating temperatures of 100 to 160°C, more preferably 110 to 140°C, are suitable for such development. Higher or lower temperatures can be selected within the above-described range, shortening or prolonging the developing time respectively. The developing time is usually from 1 second to 60 seconds. The material can be heated, for example, by being brought into contact with a heating plate or the like or with a heated drum, or, in some cases, by being passed through heated space, or by using high-frequency induction heating or a laser beam.

The present invention will now be illustrated in greater detail by reference to the following examples of preferred embodiments. Unless otherwise indicated, all parts, percentages and ratios are by weight.

EXAMPLE 1.

3.4 Grams of behenic acid was dissolved in 100 ml of toluene at 60°C, and the solution temperature was held to 60°C. Then, 100 ml of a dilute nitric acid aqueous solution of a pH of 2.0 (at 25°C) was mixed thereinto with stirring. This solution mixture was maintained at 60°C, and to this was added, while continuing the stirring, an aqueous solution prepared by adding aqueous ammonia to about 80 ml of an aqueous solution containing 1.7 g of silver nitrate to form a silver ammonium complex salt and making the total amount 100 ml with water. Thus, a dispersion containing fine crystals of silver behenate was obtained. Upon leaving this dispersion for 20 minutes at room temperature (about 20—30°C), it separated into an aqueous phase and a toluene phase.

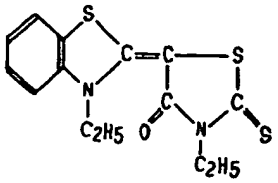
First, the aqueous phase was removed. Then, 400 ml of fresh water was added thereto for washing followed by decanting. This procedure was repeated 3 times. Then, 400 ml of water was added thereto and silver behenate was collected by centrifuging. Thus, 4 g of rod-shaped silver behenate crystals of about 1 micron in length and about 0.05 micron in width were obtained. 2.5 Grams of the thus obtained silver behenate was added to 20 ml of an isopropyl alcohol solution containing 2 g of polyvinyl butyral and was subjected to ball milling for 1 hour to

prepare a polymer dispersion. To 20 ml of this polymer dispersion of the silver salt were added the following components to prepare a thermally developable light-sensitive composition. This composition was then applied to a polyethylene terephthalate film support in a silver amount of 1.5 g per $1m^2$ of the support to prepare a thermally developable Light-sensitive Material (A).

Ammonium bromide (2.5% by weight methanol solution)	1 ml
Compound (1) (0.025% by weight 2-methoxy-ethanol solution)	1 ml
2,2'-Methylene*bis*(6-*t*-butyl-4-methyl-phenol) (25% by weight solution in 2-methoxy-ethanol)	3 ml
Phthalazinone (2.5% by weight solution in 2-methoxy-ethanol)	1 ml
Tetrachlorophthalic anhydride (0.6% by weight methanol solution)	1 ml

Separately, for the purpose of comparison, there were prepared in a similar manner a thermally developable Light-sensitive Material (B) not containing Compound (1), the sensitizer according to the present invention, and a thermally developable Light-sensitive Material (C) containing as a sensitizing dye a merocyanine dye (represented by the following formula) in place of Compound (1) in the same amount.

Merocyanine Dye:



On each of these Light-sensitive Materials (A) to (C) was top-coated a 15% by weight tetrahydrofuran solution of vinyl chloride-vinyl acetate copolymer (comprising 95% by weight of vinyl chloride and 5% by weight of vinyl acetate) in a dry thickness of 10 microns.

Each of these Light-sensitive Materials (A) to (C) was exposed to 240,000 lux-sec from a tungsten light source through an optical wedge. Thereafter, the materials were heated at 120°C for 10 seconds to develop, then the resulting blackened density was measured.

The reciprocal number of exposure amount necessary to provide a density higher than fog (transmittance at the unexposed area upon heating) by 0.1 was selected to express the sensitivity. The results obtained are shown below wherein the relative sensitivity of the Light-sensitive Material (B) was taken as 100.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	20,000	100	500

From the above-described results, it can be seen that the sensitizing agent of the present invention exhibits an outstanding sensitizing effect.

EXAMPLE 2.

The same procedures as described in Example 1 were conducted except for using both Compound (1) and the merocyanine dye used in Example 1 in the same amounts in place of Compound (1). The results obtained are shown below.

	Light-sensitive Material (A) (containing compound (1) and the merocyanine dye	Light-sensitive Material (B) (containing neither Compound (1) nor merocyanine dye)	Light-sensitive Material (C) (containing the merocyanine dye)
Relative Sensitivity	25,000	100	500

It can be seen from the results, that the combined use of Compound (1) and the merocyanine dye served to obtain an even more excellent effect.

EXAMPLE 3.

The same procedures as described in Example 1 were conducted except for using Compound (21) in place of Compound (1) in the same amount. Thus, the following results were obtained.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	5,200	100	500

The same effect as in Example 1 was observed.

EXAMPLE 4.

The same procedures as described in Example 1 were conducted except for using Compound (7) in place of Compound (1). The results obtained are as follows.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	3,800	100	500

EXAMPLE 5.

11 Grams of lauric acid was dissolved in 100 ml of butyl acetate and, while maintaining the solution at 10°C, 100 ml of aqueous nitric acid (pH at 25°C: 2.0) was added thereto with stirring. Then, while continuing the stirring, 50 ml of an aqueous solution (cooled to 0°C) of a silver nitrate ammonium complex salt containing 8.5 g of silver nitrate was added thereto over a 1 minute period to react the lauric acid with the silver ion. Thus, rod-shaped silver laurate crystals of about 1 micron in length and about 0.05 micron in width were obtained. The resulting silver salt was washed successively, with water and methanol. Thereafter, 3.0 g of polyvinyl butyral and 20 ml of isopropyl alcohol were added to 2.7 g of silver laurate and dispersed using a ball mill to prepare a polymer dispersion of the silver salt.

To 20 ml of this polymer dispersion of the silver salt were added the following components to prepare a thermally developable light-sensitive composition. The resulting composition was applied to a polyethylene terephthalate film support in a silver amount of 1.7 g per 1 m^2 of the support to prepare a thermally developable light-sensitive material (A).

Ammonium bromide (2.5% by weight methanol solution)	1 ml
Compound (20) (0.025% by weight 2-methoxy-ethanol solution)	1 ml
p-Phenylphenol (70% by weight 2-methoxy-ethanol solution)	3 ml
Phthalazinone (2.5% by weight 2-methoxy-ethanol solution)	1 ml

Tetrachlorophthalic anhydride (0.6% by weight methanol solution)	1 ml

Separately, for the purposes of comparison, there were prepared in a similar manner a thermally developable Light-sensitive Material (B) not containing Compound (20) and a thermally developable Light-sensitive Material (C) containing as a sensitizing dye a merocyanine dye (the same dye as used in Example 1) in place of Compound (20) in the same amount.

One each of these Light-sensitive Materials (A) to (C) was top-coated a 15% by weight tetrahydrofuran solution of vinyl chloride-vinyl acetate copolymer (comprising 95% by weight of vinyl chloride and 5% by weight of vinyl acetate) in a dry thickness of 10 microns.

Each of these three Light-sensitive Materials (A) to (C) was exposed to a tungsten light source through an optical wedge to impart thereto an exposure of 240,000 lux·sec. Thereafter, the materials were heated at 120°C for 10 seconds to develop, and then the resulting blackened density was measured.

The relative sensitivity was determined in the same manner as in Example 1. The results thus obtained are shown in the following table.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	4,700	100	500

From the above-described results, it can be seen that the sensitizing agent according to the present invention shows an outstanding effect.

EXAMPLE 6.

The same procedures as described in Example 5 were conducted except for using Compound (18) in place of Compound (20) in the same amount. The results thus obtained are given in the following table.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	1,200	100	500

The same effect as in Example 5.

EXAMPLE 7.

The same procedures as described in Example 5 were conducted except for using Compound (4) in place of Compound (20) in the same amount. The results thus obtained are given in the following table.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	1,400	100	500

The same effect as in Example 5 was observed.

EXAMPLE 8.

6 Grams of benzotriazole was dissolved in 100 ml of isoamyl acetate at 50°C, and the solution was cooled to −15°C. To this solution was added, under stirring, an aqueous solution prepared by dissolving 8.5 g of silver nitrate in 100 ml of dilute nitric acid solution (pH at 25°C: 2.0) and the mixture was adjusted to a temperature of 3°C. Thus, a dispersion containing fine crystals of the silver salt of benzotriazole was obtained. Upon leaving this dispersion for 20 minutes at an room temperature, it separated into an aqueous phase and an isoamyl acetate phase.

First, the aqueous phase was removed. Then, 400 ml of fresh water was added thereto for washing followed by decanting. This procedure was repeated 3 times. Then, 400 ml of water was added thereto and the silver salt of benzotriazole was collected by centrifuging. Thus, 8 g of almost spherical grains of about 1 μ in diameter of the silver salt of benzotriazole were obtained. 2.5 Grams of the thus

obtained silver salt of benzotriazole was added to 40 ml of an isopropyl alcohol solution containing 4 g of polyvinyl butyral and was subjected to ball milling for 4 hours to prepare a polymer dispersion of the silver salt. To 40 ml of this polymer dispersion of the silver salt were added the following components to prepare a thermally developable light-sensitive composition. This composition was then applied to a polyethylene terephthalate film support in a silver amount of 1.2 g per 1 m^2 of the support to prepare a thermally developable Light-sensitive Material (A).

Ammonium Iodide (8.5% by weight methanol solution)	1 ml
Solution containing 2 g of Ascorbic Acid Monopalmitate and 2 g of Ascorbic Acid Dipalmitate in 10 ml of 2-methoxy-ethanol	10 ml
Compound (8) (0.2% by weight 2-methoxy-ethanol solution)	1 ml
N-Ethyl-N'-dodecylurea (2.5% by weight 2-methoxy-ethanol solution)	2 ml

Separately, for the purposes of comparison, there were prepared in the same manner a thermally developable Light-sensitive Material (B) not containing Compound (8) and a thermally developable Light-sensitive Material (C) containing as a sensitizing dye a merocyanine dye (the same dye as described in Example 1) in place of Compound (8) in the same amount.

On each of these Light-sensitive Materials (A) to (C) top-coated a 15% by weight tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (comprising 95% by weight of vinyl chloride and 5% by weight of vinyl acetate) in a dry thickness of 8 microns.

Each of these Light-sensitive Materials (A) to (C) was exposed to a tungsten light source through an optical wedge to impart thereto an exposure of 1,200,000 lx·sec. Thereafter, the materials were heated at 130°C for 30 seconds to develop. Then, the resulting blackened density was measured. The relative sensitivity was determined in the same manner as described in Example 1. The results thus obtained are tabulated below.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	450	100	150

From the above-described results, it can be seen that the sensitizer according to the present invention shows an outstanding effect.

EXAMPLE 9.

The same procedures as described in Example 8 were conducted except for using Compound (3) in place of Compound (8) in the same amount. Thus, the results as given in the following table were obtained.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	400	100	150

The same effect as in Example 8 was observed.

EXAMPLE 10.

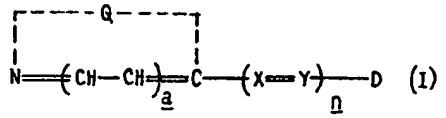
The same procedures as described in Example 8 were conducted except for using Compound (13) in place of Compound (8) in the same amount. Thus, the results as given in the following table were obtained.

	Light-sensitive Material (A)	Light-sensitive Material (B)	Light-sensitive Material (C)
Relative Sensitivity	390	100	150

The same effect as in Example 8 was observed.

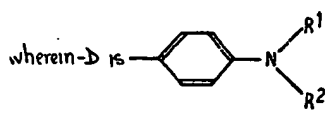
WHAT WE CLAIM IS:—

1. A heat-developable light-sensitive material comprising a support bearing:
(a) an organic silver salt,
(b) a light-sensitive silver halide, or a compound capable of forming a light-sensitive silver halide by reaction with said organic silver salt (a), in an amount effective to catalyze the reaction of compounds (a) and (c).
(c) a reducing agent capable of reducing to elemental silver the organic silver salt (a) when the material is being heated in the presence of the component (b) which has been exposed to light,
(d) a binder, which may be omitted if the organic silver salt (a) and/or the reducing agent (c) act as a binder,
(e) a quinoline compound represented by the following general formula (I):

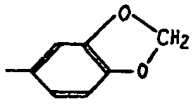


(I)

wherein D is



or



R^1 and R^2 being each independently an alkyl group having from 1 to 4 carbon atoms or a benzyl group; X and Y are each independently $=\overset{H}{C}-$ or $=N-$; n is 1 or 2; a is 0 or 1; and Q represents the atoms necessary to complete a quinoline nucleus which may be further substituted; or (e) may be a quinoline ring N-oxide derived from said quinoline compound or a quinolinium salt dervied from said quinoline compound.

2. A light-sensitive material as claimed in Claim 1, wherein R^1 and/or R^2 is methyl, ethyl or *n*-propyl.

3. A light-sensitive material as claimed in Claim 1 or 2, wherein component (e) is 4-(*p*-dimethylaminostyryl)quinoline, 2-(*p*-dimethylaminostryryl)-6-dimethylaminoquinolinium ethyl iodide, 4-(*p*-dimethylaminostyryl)quinolinium *n*-heptyl iodide, 4-(3,4-dioxymethylenephenylethylenyl)quinolinium ethyl iodide, or 4-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]quinolinium *n*-heptyl iodide.

4. A light-sensitive material as claimed in any preceding claim, wherein component (e) is present in an amount of 10^{-6} to 10^{-2} mol per mol of said organic silver salt (a).

5. A light-sensitive material as claimed in any preceding claim, wherein said support bears a cyanine dye or a merocyanine dye.

6. A light-sensitive material as claimed in Claim 6, wherein said cyanine dye or said merocyanine dye is present in an amount of 10^{-6} to 10^{-2} mol per mol of said organic silver salt (a).

7. A light-sensitive material as claimed in any preceding claim, wherein said organic silver salt (a) is a silver salt of an organic carboxylic acid or of an organic compound containing an imino group or a mercapto group.

8. A light-sensitive material as claimed in any preceding claim, wherein said compound capable of forming a light-sensitive silver halide by reaction with said organic silver salt (a) is a hydrogen halide, an ammonium halide or a metal halide, the halide being chloride, bromide or iodide.

9. A light-sensitive material as claimed in Claim 8, wherein said metal halide is the chloride, bromide or iodide of strontium, cadmium, zinc, tin, chromium, sodium, barium, iron, caesium, lanthanum, copper, calcium, nickel, magnesium,

potassium, aluminium, antimony, gold, cobalt, mercury, lead, beryllium, lithium, manganese, gallium, indium, platinum, thallium or bismuth.

10. A light-sensitive material as claimed in any of Claims 1 to 7, wherein said compound capable of forming a light-sensitive silver halide by reaction with said organic silver salt (a) is monochlorotriphenylmethane, mon bromotriphenylmethane, 2-bromo-2-methylpr pane, 2-bromo-butyric acid, 2-bromoethanol, dichlorobenzoph none, triiodomethane, tribromomethane or tetrabromomethane.

11. A light-sensitive material as claimed in any preceding claim, wherein said light-sensitive silver halide is silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide or silver iodide.

12. A light-sensitive material as claimed in any preceding claim, wherein said reducing agent (c) is a substituted phenol, a substituted or unsubstituted bisphenol, a substituted or unsubstituted naphthol or bis-naphthol, a di- or poly-hydroxynaphthalene, di- or higher- polyhydroxybenzene, di- or higher- polyhydroxynaphthalene, a hydroquinone mono-, di-, tri- or tetra-ether, ascorbic acid or a derivative thereof, a 3-pyrazolidone, a pyrazolin-5-one, a reducing sugar, kojic acid or hinokitiol.

13. A heat-developable light-sensitive material as claimed in Claim 1 and substantially as hereinbefore described with reference to and as shown in any one of Examples 1 to 10.

14. A method of developing a light-sensitive material as claimed in any preceding claim, which material has been imagewise-exposed, comprising heating the material to a temperature for a duration until a black image is obtained.

15. A method as claimed in Claim 14, wherein the temperature is from 100° to 160°C.

16. A method as claimed in Claim 15, wherein the temperature is from 110° to 140°C.

17. A method as claimed in any of Claims 14 to 16, wherein the duration is from 1 to 60 seconds.

18. A material bearing a visible image developed by a process as claimed in any of Claims 14 to 17.

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